Synthesis and Photo-physical Properties of Carbazole and Benzimidazole based Fluorescent Derivatives

A Thesis
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by

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Affectionately
dedicated
to my loving
Parents, Dikshil
and
Almighty

Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis entitled "**Synthesis and Photo-physical Properties of Carbazole and Benzimidazole based Fluorescent Derivatives**" is the result of investigations carried out by me in the ***School of Basic Sciences,*** Indian Institute of Technology Mandi, under the supervision of ***Dr. Pradeep C. Parameswaran*** and ***Dr. Abhimanew Dhir,*** and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigators.

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Abbreviations

EM ……..…...electromagnetic

Φ……..……..…… quantum yield

ED……..……..……...electron donor

D……..……...……..donor

A……..…….……acceptor

UV……..……..……ultraviolet

Vis……...visible

ACQ……..aggregation caused quenching

AIEE……aggregation induced emission enhancement

T_g…….……..glass transition temperature

m.p……..……..melting point

°C……..degrees Celsius

DCM…….……...dichloromethane

DMF…….....dimethylformamide

DMSO……...dimethylsulfoxide

THF…….……tetrahydrofuran

ESI…….……electron spray ionization

HRMS…….……high resolution mass spectrometry

µM……...……micromolar

NMR……..nuclear magnetic resonance

HOMO……highest occupied molecular orbital

LUMO…….lowest unoccupied molecular orbital

TD-DFT…….time-dependent density functional theory

λ……..……wavelength

τ……..……..tau

XRD……..……..…X-ray diffraction

v……...……...volume

TEM……...…….……transmission electron microscopy

ORTEP……..……..……..…oak ridge thermal ellipsoid plot

ns……..……..…..……nano seconds

nm..……..……..…..……nano meter

min…….……..……...minute

ml……..……..……..milliliter

mg……..……..…..……..milligram

EDX……..……...…….……...energy dispersive analysis of X-rays

SEM……..……. scanning electron microscopy

CCDC…….……...…….…..cambridge crystallographic data centre

TGA…….……..thermo gravimetric analysis

mmol…… millimoles

h……..hour

MeOH…….……methanol

KBr…….……...potasium bromide

μM ……..micromolar

λ_{ex} …….……..excitation wavelength

λ_{em} ……..……..emission wavelength

$\bar{\nu}$……..……wavenumber

Å……..angstrom

m/z……mass-to-charge ratio

Materials, methods and instrumentation

All reagents were purchased from Sigma Aldrich and were used without further purification. THF and H_2O (buffered to pH 7.1) were used to perform analytical studies. All the fluorescence spectra were recorded on Agilent Technologies Cary Eclipse fluorescence spectrometer. UV-Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer and FT-IR spectra were recorded on PerkinElmer FT-IR spectrometer (Spectrum Two, Serial No:88689) and on Agilent technologies cary 600 series. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer and JEOL 500 NMR spectrometer using $CDCl_3$, DMSO as solvents and TMS as internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d= doublet, br = broad singlet, m = multiplet), coupling constant, J (Hz) integration, and interpretation. Mass spectra were recorded on Bruker HD compact mass spectrometer. TEM characterization has been done by SEI TECNAI F 20 DST sponsored high resolution transmission electron microscopy (HRTEM) for the 2nd chapter and was done by using FEI TECNAI G2 20 –TWIN 200KV high resolution transmission electron microscopy (HRTEM) for the rest of the chapters. SEM characterization was done by using an FEI-Nova nano SEM-450. The fluorescence life time were measured by using LASER diode from HORIBA instrument. Elemental analysis was done by Thermo-Flash 2000. Confocal images were taken in Nikon eclipse Ti inverted microscope at 60× (oil merging) using 401 nm laser. Solid state quantum yields were calculated on a Horiba Scientific Fluorolog-3. TGA studies were done using a NETZCH STA449 F1 instrument. The electrochemical voltammetry (CV) was performed using a Metrohm Autolab electrochemical workstation in 0.1 M tetrabutylammonium perchlorate (Bu_4ClO_4) solution. Single crystal X-ray details along with CCDC numbers are given in

respective chapters. Powder X-ray diffraction (PXRD) data was collected on Rigaku Smart Lab 9 KW rotating anode Powder X-ray diffractometer at room temperature.

Preparation of HEPES solution of pH = 7.1

To prepare 1 L HEPES buffer of 7.1 pH add 11.92 g of HEPES, 11.0 ml of 1 M NaOH and 89.0 ml of 1 M NaCl and dilute it to 1 L by adding distilled water.

All the solvents were of spectroscopic grade and were used without further purification. Nitrate and chloride salts of Na^{+}, K^{+}, Mg^{2+}, Al^{3+}, Ca^{2+}, Ni^{2+}, Cr^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+}, Hg^{2+} were used for spectroscopic studies. Further, tetrabutylammonium salts of PO_4^{3-}, OAC^{-}, NO_3^{2-}, F^{-}, ClO_4^{-}, SCN^{-}, Cl^{-}, Br^{-}, SO_4^{2-} and CN^{-} were used.

Computational studies

The theoretical calculations were carried out using the Gaussian 09. The structure optimization was done by using density functional theory (DFT) method. All the DFT calculations were performed in gas phase with hybrid B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) function. The 6-31G (d,p) basic set was used for C, H, N and O atom. The molecular orbital contours were plotted using chemcraft.

Quantum yield

Fluorescence quantum yield was determined using quinine sulphate ($\Phi_{F(R)}$= 0.54) in 1N H_2SO_4 as standard. An excitation wavelength of 352 nm from a xenon spectroflurophotometer was used. The quantum yield was calculated by using equation (1), in which $\Phi_{F(S)}$ is the radiative quantum yield of sample, $\Phi_{F(R)}$ is the radiative quantum yield of reference, A_R and A_S are the absorbance of reference and the sample, respectively, F_R and F_S the area of emission for reference and the sample, respectively, n_R and n_S are the refractive indices of the reference and sample solutions, respectively.

Equation 1

$$\Phi_{F(S)} = (A_R / A_S) (F_S / F_R) (n_S / n_R)^2 \Phi_{F(R)}$$

Solid-state quantum yield

Solid-state quantum efficiency was determined by the integrating sphere technique using a quanta- φ F-3029 sample chamber of the Horiba Scientific Fluorolog-3 spectrofluorometer equipped with an integrating sphere of diameter 15.2 cm coated with Spectralon material.

Detection limit

The detection limit was determined from the following Eq. 2:

$$DL = 3 \times \sigma / M$$

Where M is the standard deviation of the blank solution detected for 10 times, σ is the slope of the calibration curve.

X-ray crystallography

Single crystal X-ray data were collected with Agilent SuperNova, equipped with multilayer optics monochromated dual source (Cu and Mo) and Eos CCD detector, using Mo-Kα (0.71073 Å) radiation. Data acquisition and reduction were made using the program CrysAlisPRO.[1] The structure was solved with ShelXS[2] program and refined on F2 by full matrix least-squares techniques with ShelXL[2] program in Olex2 (v.1.2) program package.[3] Anisotropic displacement parameters were applied for all atoms, except hydrogen atoms. H atoms were calculated into their positions or located from the electron density map and refined as riding atoms using isotropic displacement parameters. The single crystal structure was solved using OLEX-2 software on Agilent single crystal XRD instrument. These data can be obtained free of charge from the cambridge crystallographic data centre via www.ccdc.cam.ac.uk/data_request/cifdata.

References:

1. CrysAlisPro Program, version171.37.33c; Agilent Technologies:Oxford, 2012.

2. G. M. Sheldrick, ActaCrystallogr., 2008, A 64, 112.

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Abstract

Fluorescence is a fast, simple and inexpensive method to determine the concentration of an analyte in solution. Fluorescent chemosensors have been reported for sensing of biologically important species such as metal ions, anions and small molecules. These chemosensors measure the change in the photo-physical properties of the system to report the presence of an analyte. The presence of an analyte can be detected via quenching or enhancement of fluorescence signal. The organic molecules emitting fluorescence are known as fluorophores. We chose carbazole and benzimidazole as fluorophore for the chemosensing as carbazole has a strong π-electron conjugation and high thermal stability. It's optical and electrical properties can be easily tuned by putting various substituents at different positions. Carbazole based molecules are widely used in various areas such OLEDs, nanoparticle formation, sensing of cations, anion, and molecules. Similarly, Benzimidazole is a heterocyclic molecule incorporating an imidazole and benzene ring. Because of their emissive properties benzimidazole derivatives have been commonly used as probe for recognition of all cations, anions and neutral molecules. Benzimidazole based molecules possess distinctive linear and non-linear optical properties and have an outstanding thermal stability in guest–host systems. Benzimidazole derivatives have also an important role as pharmacophore in medicinal chemistry.

The key feature of chemosensors is to detect analytes like cations, anions and small molecules and consecutively induce a recognition–transduction signal. The development of chemosensors occurs by the combination of mainly two units i.e. the binding site and the signaling subunit. Functionalization of chemosensors enables it to undergo various binding phenomenon which can be detected with different signaling mechanisms viz. PET, ICT, TICT, Excimer, ESIPT, FRET, AIEE in fluorescence spectroscopy.

Recently, aggregation induced emission enhancement (AIEE) materials have been used for fluorescent detection of environmentally and biologically significant ions and molecules. AIEE is an unusual phenomenon in which organic luminophores show higher luminescence in the aggregated state than in solution. The AIEE phenomenon basically works on the synergistic effect of restricted intramolecular rotation (RIR) and twisted molecular conformation. In the present thesis, we designed and synthesized new fluorescent carbazole based derivatives exhibiting phenomenon of aggregation induced emission enhancement (AIEE). We have also synthesized benzimidazole based derivatives exhibiting phenomenon of twisted state intramolecular charge transfer (TICT) and sensing analyte through chemosdosimetry approach. The work is distributed in six different chapters from chapter 2 to chapter 7 excluding chapter 1 and chapter 8 which includes introduction and conclusion respectively.